# REGENERATION OF Pt/KL CATALYSTS UTILIZED FOR n-OCTANE AROMATIZATION



Ms. Dholporn Lertkijcharoenwong

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2003

ISBN 974-17-2279-6

Thesis Title:

Regeneration of Pt/KL Catalysts Utilized for n-Octane

Aromatization

By:

Ms. Dholporn Lertkijcharoenwong

Program:

Petrochemical Technology

Thesis Advisors:

Prof. Somchai Osuwan

Assoc. Prof. Thirasak Rirksomboon

Prof. Daniel E. Resasco

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

K. Bunyaln'at. College Director

(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

(Prof. Somchai Osuwan)

(Assoc. Prof. Thirasak Rirksomboon)

(Prof. Daniel E. Resasco)

(Assoc. Prof. Sumaeth Chavadej)

(Dr. Boonyarach Kitiyanan)

Boonyarach Kitiyanan

### **ABSTRACT**

4471008063 : PETROCHEMICAL TECHNOLOGY PROGRAM

Ms. Dholporn Lertkijcharoenwong: Regeneration of Pt/KL

Catalysts utilized for *n*-Octane Aromatization.

Thesis Advisors: Prof. Daniel E. Resasco, Prof. Somchai Osuwan,

and Assoc. Prof. Thirasak Rirksomboon, 50 pp. ISBN 974-17-

2279-6

Keywords : Regeneration/ Aromatization / n-Octane/ Pt/K-LTL / Vapor phase

impregnation/ Dehydrocyclization/ DRIFTS.

Aromatization is one of the most important petrochemical processes for aromatic production. Pt/KL catalyst prepared by Vapor Phase Impregnation method is known to be an effective catalyst for n-octane aromatization. However, during the reaction, catalysts deactivate due to coke formation. Consequently, it is common practice to regenerate the catalysts to recover their activity. Hence, the attempt of this work is to investigate the influences of air flow rate, temperature and time of regeneration by coke oxidation in air to determine the optimal regeneration conditions of such catalysts. In addition, oxychlorination treatment was also studied to redisperse Pt particles after regeneration in air. It was found that the optimal regeneration temperature, time and air flow rate was 250°C, 0.5 h and 100 ml/min/g. of catalysts, respectively. Moreover, it was clearly seen that regeneration with oxychlorination treatment can restore Pt redispersion as close as that of the fresh catalysts.

## บทคัดย่อ

คลพร เลิศกิจเจริญวงศ์: รีเจนเนอเรชันของตัวเร่งปฏิกิริยาแพลตินัม/โพแทสเซียมซีโอ ไลต์แอลซึ่งใช้สำหรับปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทน (Regeneration of Pt/KL Catalysts utilized for *n*-Octanes Aromatization) อ. ที่ปรึกษา: ศ.คร. แคเนียล อี รีซัสโก ศ. คร. สมชาย โอสุวรรณ และ รศ.คร. ธีรศักดิ์ ฤกษ์สมบูรณ์ 50 หน้า ISBN 974-17-2279-6

ปฏิกิริยาอะโรมาไทเซชันเป็นปฏิกิริยาสำคัญปฏิกิริยาหนึ่งในการผลิตสารอะโรมาติกซ์ ตัวเร่งปฏิกิริยาแพลทินัมบนซีโอไลต์แอล (Pt/KL) ซึ่งเตรียมโดยวิธีระเหิดสารประกอบโลหะ แพลทินัมเข้าไปยังโพรงของซีโอไลต์ (vapor phase impregnation) ได้รับการขอมรับว่าเป็นตัว เร่งปฏิกิริยาที่มีประสิทธิภาพสำหรับปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทน อย่างไรก็ตาม ในระหว่างการเกิดปฏิกิริยา ความว่องไวในการทำปฏิกิริยาลดลงเนื่องจากการเกิดโล้ก ตังนั้นจึง ด้องเร่งตัวเร่งปฏิกิริยาเพื่อคืนสภาพความว่องไวในการทำปฏิกิริยา งานวิจัยนี้จึงมีจุดประสงค์เพื่อ ศึกษาผลกระทบของความเร็วของอากาศ, อุณหภูมิ และเวลาที่ใช้ในการปรับสภาพด้วยวิธีโล้ก ออกซิเดชันในอากาศ เพื่อหาสภาวะการปรับสภาพที่เหมาะสมของตัวเร่งปฏิกิริยาดังกล่าว นอก จากนี้ยังได้มีการศึกษาการทำออกซีคลอรีเนชัน (Oxychlorination Treatment) เพื่อคืนการ กระจายอนุภาคแพลทินัมหลังจากการปรับสภาพในอากาศ ผลการศึกษาพบว่าสภาวะอุณหภูมิ, เวลาที่ใช้ และความเร็วของอากาศที่เหมาะสมคือ 250 เซลเซียส, 0.5 ชั่วโมง และ 100 มิลลิลิตร/ นาที/กรัมของตัวเร่งปฏิกิริยาตามลำดับ นอกจากนี้ได้พบว่าการปรับสภาพที่มีการทำออกซีคลอรีเนชันสามารถคืนการกระจายอนุภาคแพลทินัมของตัว เร่งปฏิกิริยาใหม่

#### **ACKNOWLEDGEMENTS**

This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

I would like to express my gratitude to my advisors, Dr. Somchai Osuwan, Dr. Daniel E. Resasco, and Dr. Thirasak Rirksomboon for their useful guidance. I really appreciate working with them.

I would like to thank to the PPC's faculty, all of my friends, and all of Ph.D. students for their willing cooperation especially Dr. Siriporn Jongpatiwut for her helpful guidance and encouragement.

I would like to acknowledge Dr. Sumaeth Chavadej and Dr. Boonyarach Kitiyanan for serving on my thesis committee and for their comments.

I would like to extend special thanks to PPC's staff for their contributions, particularly Mr. Chaturong Tiamsiri for all mechanical work and C. P. O. Poon Arjpru for all electronic work.

Finally, I would like to express my gratitude to my family, who play the greatest role in my success, for their endless love and encouragement.

## **TABLE OF CONTENTS**

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	iv
	Acknowledgement	V
	Table of Contents	vi
	List of Tables	viii
	List of Figures	ix
	Abbreviations	xii
CHAPTER		
I	INTRODUCTION	1
II	LITERATURE SURVEY	3
	2.1 Catalyst for <i>n</i> -Octane Aromatization	3
	2.2 Catalyst Deactivation	6
	2.3 Catalyst Regeneration	7
III	EXPERIMENTAL	10
	3.1 Materials	10
	3.1.1 Chemicals	10
	3.1.2 Gases	10
	3.2 Catalyst Preparation via Vapor-Phase Impregnation Method	10
	3.2.1 Calcination of KL Zeolite	10
	3.2.2 Loading Pt	11
	3.3 Reaction and Regeneration	11
	3.3.1 Catalyst Reduction	11
	3.3.2 Reaction Testing	11
	3.3.3 Regeneration in Air	12
	3.3.4 The Product of <i>n</i> -Octane Aromatization Analysis	13

CHAPTER			PAGE
	3.3.5	Pt Redispersion	13
	3.4 Chara	cterization of Catalysts	14
	3.4.2	Fourier Transform-Infrared Spectroscopy	
		of Adsorbed CO	14
	3.4.3	Temperature Programmed Oxidation (TPO)	14
IV	RESULT	S AND DISCUSSION	17
	4.1 The R	Regeneration in Air of Pt/KL Catalysts	17
	4.1.1	Effect of Regeneration Temperature	17
		4.1.1.1 Catalytic Activity Measurement	17
		4.1.1.2 Characterization of Catalysts	22
	4.1.2	Effect of Regeneration Time	27
		4.1.2.1 Catalytic Activity Measurement	27
		4.1.2.2 Characterization of Catalysts	31
	4.1.3	Effect of Air Flow Rate	33
		4.1.3.1 Catalytic Activity Measurement	33
		4.1.3.2 Characterization of Catalysts	37
	4.2 Pt Red	dispersion Study	40
V	CONCLU	USIONS AND RECOMMENDATIONS	42
	REFERE	NCES	43
	APPEND	ICES	46
	Appendix	A Structure of Zeolite	46
	Appendix	B TPO profile of regenerated Pt/KL after	
		regeneration in air	47
	Appendix	C Standard deviation (SD)	49
	CURRIC	IILIIM VITAE	50

## LIST OF TABLES

TABLE	
Regeneration procedures	12
TPO characterization of spent and regenerated Pt/KL catalysts at	
different regeneration temperatures	26
TPO characterization of spent and regenerated Pt/KL catalysts at	
different regeneration times	32
TPO characterization of spent and regenerated Pt/KL catalysts at	
different air flow rates	38
Product distribution of <i>n</i> -octane aromatization	
over Spent Pt/KL catalysts	39
	Regeneration procedures TPO characterization of spent and regenerated Pt/KL catalysts at different regeneration temperatures TPO characterization of spent and regenerated Pt/KL catalysts at different regeneration times TPO characterization of spent and regenerated Pt/KL catalysts at different air flow rates Product distribution of <i>n</i> -octane aromatization

# LIST OF FIGURES

FIGUR	FIGURE	
3.1	Experimental set up	15
3.2	Pt redispersion set up (in hood)	16
4.1	The variation of <i>n</i> -octane conversion without regeneration in air	18
4.2	The variation of <i>n</i> -octane conversion with regeneration in air	10
	of various regeneration temperature; operated at regeneration	
	time = $0.5$ h, air flow rate = $100$ ml/min/g.	18
4.3	The average value of conversion of various regeneration temperature	
	(150-400°C) after regeneration in air	20
4.4	The average value of total aromatics selectivity of various	
	regeneration temperature (150-400°C) after regeneration in air	20
4.5	The average value of C <sub>8</sub> aromatics yield of various regeneration	
	temperature (150-400°C) after regeneration in air	21
4.6	The average value of EB/OX ratio of various regeneration	
	temperature (150-400°C) after regeneration in air	21
4.7	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	catalysts after reaction-regeneration cycles at 150°C of regeneration	
	temperature	23
4.8	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	catalysts after reaction-regeneration cycles at 200°C of regeneration	
	temperature	23
4.9	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	catalysts after reaction-regeneration cycles at 250°C of regeneration	
	temperature	24
4.10	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	catalysts after reaction-regeneration cycles at 300°C of regeneration	
	temperature	24

FIGUR	GURE	
4.11	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	catalysts after reaction-regeneration cycles at 400°C of regeneration	
	temperature	25
4.12	Average value of C <sub>8</sub> aromatics yield of various regeneration time	
	(0.5-8 h) after regeneration in air	28
4.13	Average value of aromatics selectivity of various regeneration time	
	(0.5-8 h) after regeneration in air	28
4.14	Average value of conversion of various regeneration time	
	(0.5-8 h) after regeneration in air	29
4.15	Average value of EB/OX ratio of various regeneration time	
	(0.5-8 h) after regeneration in air	29
4.16	Average value of B/C <sub>8</sub> aromatics ratio of various regeneration	
	time (0.5-8 h)	30
4.17	EB and OX selectivity of various regeneration time (0.5-8 h)	
	after regeneration in air	30
4.18	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	for regeneration time of 0.5, 2 and 8 h	31
4.19	Average value of C <sub>8</sub> aromatics after regeneration in various	
	air flow rate (50-200 ml/min/g)	33
4.20	Average value of aromatics selectivity after regeneration in various	
	air flow rate (50-200 ml/min/g)	34
4.21	Average value of conversion ratio after regeneration in various	
	air flow rate (50-200 ml/min/g)	34
4.22	Average value of EB/OX ratio after regeneration in various	
	air flow rate (50-200 ml/min/g)	35
4.23	Average value of B/C <sub>8</sub> aromatics ratio after regeneration in various	
	air flow rate	36
4.24	EB and OX selectivity of different air flow rate (50-200 ml/min/g)	
	After regeneration in air	36

FIGUR	E	PAGE
4.25	DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL	
	for regeneration time of 50, 100 and 200 ml/min/g	37
4.26	DRIFTS of adsorbed CO spectra after regeneration in air of fresh and	
	regenerated Pt/KL catalysts with and without Pt redispersion at	
	regeneration temperature of 150°C	40
4.27	DRIFTS of adsorbed CO spectra after regeneration in air of fresh and	
	regenerated Pt/KL catalysts with and without Pt redispersion at	
	regeneration temperature of 400°C	41

#### **ABBREVIATIONS**

Pt/KL Platinum supported on KL zeolite

VPI Vapor-phase impregnation

DRIFTS Diffuse Reflectance Infrared Fourier Transform Spectroscopy

of Adsorbed CO

TPO Temperature programmed oxidation

GC Gas chromatograph

WHSV Weigh hourly space velocity

TOS Time on stream

B Benzene

EB Ethylbenzene

OX o-Xylene PX p-Xylene

MX m-Xylene

 $C_8$  Arom  $C_8$  aromatics

Arom Aromatics

Regen@250 C Pt/KL catalyst regenerated at regeneration temperature of

250°C

Regen@2 h Pt/KL catalyst regenerated for 2 h

Regen@100ml/min/g Pt/KL catalyst regenerated in air flow rate of 100ml/min/g.